

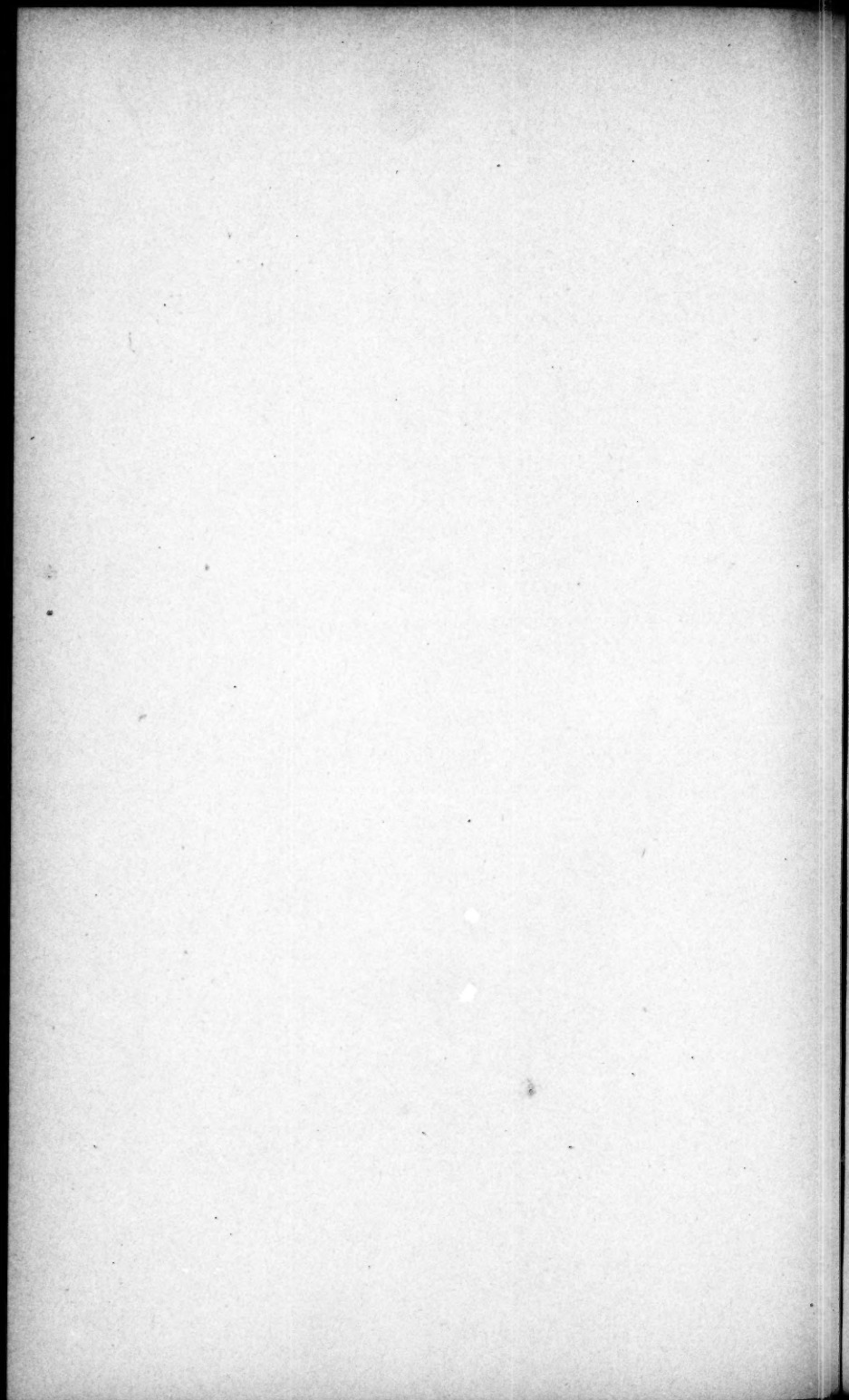
Proceedings of the American Academy of Arts and Sciences.

VOL. XLVI. No. 5. — SEPTEMBER, 1910.

CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF
PHYSICAL CHEMISTRY OF THE MASSACHUSETTS
INSTITUTE OF TECHNOLOGY. — No 59.

*THE ELECTROMOTIVE FORCE PRODUCED IN
SOLUTIONS BY CENTRIFUGAL ACTION.*

BY RICHARD C. TOLMAN.



CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF
PHYSICAL CHEMISTRY OF THE MASSACHUSETTS
INSTITUTE OF TECHNOLOGY.—No. 59.

THE ELECTROMOTIVE FORCE PRODUCED IN SOLUTIONS
BY CENTRIFUGAL ACTION.

BY RICHARD C. TOLMAN.

Presented by Professor A. A. Noyes. Received June 17, 1910.

CONTENTS.

1. Work of previous Investigators and Purpose of this Research . . .	109
2. Derivation of an Expression for the Electromotive Force	113
The Effect of Hydration	114
3. Kinetic Derivation of the Electromotive Force Expression	115
4. Description of Apparatus	117
The Steam Turbine	117
The Thrust Bearing	119
The "Spinning Top"	120
The Rotator	122
The Solution Tube	122
The Electrical Connections	124
The Mercury Contacts	125
The Magneto	126
The Electrical Measuring Instruments	126
5. The Method of Procedure	126
6. The Experimental Results	128
7. Ratio of the Electromotive Force to the Square of the Number of Revolutions per Second	131
8. The Partial Volumes of Iodine and the Iodides	131
9. Calculation of the Transference Number	140
The Accuracy of the Results	141
The Effect of Pressure on the Results	141
The Effect of the Dissolved Iodine on the Results	143
10. Comparison of the Results with other Transference Measurements	143
11. Summary	144

1. WORK OF PREVIOUS INVESTIGATORS AND PURPOSE OF THIS
RESEARCH.

If the passage of an electric current is associated with the actual transfer of matter along the conductor, a number of phenomena, de-

pending upon the inertia of this matter, are to be expected. The nature of these phenomena was completely discussed by Maxwell; but they have not yet been detected in metallic conductors.¹ In electrolytic conductors, however, the experiments of Hittorf have shown that there is an actual transfer of matter through the solution, accompanying the passage of a current. As an example of the electrical effects which may accompany such a motion of the carriers of electricity or ions, let us consider a solution of silver nitrate placed in a vertical tube with silver electrodes at the top and bottom. The passage of a current of electricity through this solution from the lower to the upper electrode will be accompanied by a raising of the silver ions in the solution and an approximately equal lowering of the considerably lighter nitrate ions. The net effect produced by the current will be the lifting of a certain weight of material from the lower electrode to the upper; and the work thus done against gravity must correspond to a definite electromotive force which will oppose the passage of the current in this direction.

Effects of this kind were first predicted by Colley,² and have also been considered by various other investigators.³ Colley himself was

¹ Maxwell, Treatise on Elec. & Mag., 3rd edition, Vol. II, 211 et seq.; Lodge, Modern Views of Elec. & Mag., 3rd edition, 89; Nichols, Phys. Zeitschr. **7**, 640 (1906).

² Colley, Journal der St. Petersburg chem. und phys. Gesellschaften **7**, 333, 1875; Pogg. Ann. **157**, 370 (1876); Ibid. **157**, 624 (1876); Wied. Beibl. **5**, 457 (1881); Wied. Ann., **17**, 55 (1882).

³ Lodge, Phil. Mag. **2**, 367 (1876); Hertz, Wied. Ann. **14**, 590 (1881); Des Coudres, Wied. Ann. **49**, 284 (1893); Ibid. **57**, 232 (1896). The electromotive force which is produced in salt solutions by the action of gravity must be carefully distinguished from the actual changes in the concentration of the solute which gravity will produce. The difference in concentration between the solution in the upper and lower ends of a vertical tube, or the central and peripheral portions of a rotating tube can be calculated from simple thermodynamic considerations. It is to be expected, however, that this difference in *concentration* will be very *slowly* established (see Des Coudres, l. c. below). The difference in *potential* between the two ends of the solution is an *immediate* phenomenon which occurs as soon as the tube is set up. It is evident that when the final change in the concentration of a salt solution has completed itself there will no longer be any potential difference between the upper and lower portion of the solution. A complete bibliography of the theoretical and experimental work which has been done in this field follows: Gay Lussac, Ann. chim. phys. **11**, 306 (1819); Gouy et Chaperon, Ann. chim. phys. **12**, 384 (1887); Nernst, Zeitschr. f. phys. Chem. **2**, 637 (1888); Duhem, Journ. de phys. **7**, 391 (1888); T. v. Turin, Journ. der russ. Geschichte, **24**, 90 (1892), Wied. Beibl. **17**, 16 (1893); Des Coudres, Wied. Ann. **49**, 284 (1893); Ibid. Wied. Ann. **55**, 213 (1895); Van der Waals, Zeitschr. f. phys.

able to detect the existence of potential differences between the upper and lower electrodes placed in solutions of silver nitrate and cadmium iodide. The small electromotive forces produced in these solutions by gravity are masked by the presence of much larger variable potential differences which are due to otherwise undetectable differences between the two electrodes used. The effect of gravity is only perceived when a series of measurements is made of the deflections of a very sensitive galvanometer, the positions of the upper and lower electrodes being interchanged between each two measurements by a reversal of the tube containing the electrolyte. The potential differences, which Colley thus found, were of the order of magnitude theoretically predicted. Later he also showed the presence of a momentary electromotive force produced by the sudden stopping of a falling tube containing cadmium iodide solution.

The experimental problem was next attacked by Des Coudres who substituted centrifugal force for the weaker action of gravity. He made use of a rotating apparatus in which were placed two tubes with electrodes connected in series, containing cadmium iodide solution. The electrodes were placed 31 cm. and 9 cm. from the center and at 5.8 revolutions per second he obtained an electromotive force of 155 microvolts. Individual measurements, however, varied at times more than 10% from the mean. Although the substitution of centrifugal force for the force of gravity greatly increases the size of the effect which can be obtained, it is accompanied by the introduction of new errors, produced, for example, by the unequal heating of the central and peripheral portions of the apparatus, as well as by other difficulties. The method was abandoned by Des Coudres in favor of measurements on specially constructed gravity cells. These measurements are of a considerable degree of accuracy and the results will be given in detail.

As we shall see in the next section, it is possible to derive a relation connecting the electromotive force produced by the action of gravity and the transference number of the electrolyte. The measurements of Des Coudres were made for the purpose of comparing the transference

Chem. 5, 157 (1890); Bredig *Zeitschr. f. phys. Chem.* 17, 459 (1895); Lobry de Bruyn et van Calcar, *Red. d. travaux chim. d. Pays-Bas*, 23, 218 (1904); Franklin & Freudenberger, *Trans. Am. Electrochem. Soc.* 8, 29 (1905); Earl of Berkeley & C. V. Burton, *Phil. Mag.* 17, 606 (1909); Gibbs, *The Scientific Papers of*, Longmans, Green & Co. (1906), Vol. I, 144.

As to experimental results it may be said that the work of van Calcar and de Bruyn is in complete disagreement with the theory. The result reported by the Earl of Berkeley and Dr. Burton is, however, of the predicted order of magnitude.

numbers calculated from electromotive force with those determined by the Hittorf method. In his first gravitational experiment he again made use of cadmium iodide solution which owing to complex ion formation apparently has a transference number greater than unity, and hence gives a large electromotive force. In the experiment the solution was placed in a glass tube with the electrodes at the two ends about 91 cm. apart. The gravitational electromotive force was deduced from a series of readings of galvanometer deflection, the positions of the upper and lower electrodes being interchanged between each two measurements. The transference number of the solution was found by calculation to be 1.236, differing by at least five per cent from that determined in the analytical way.

In order to test the theory on more simple solutions such as the chlorides of the alkali metals, which do not have abnormal values of the transference number, it was necessary to compensate for the decreased size of the effect by the construction of an apparatus with greater difference in height between the electrodes. The electrodes were placed in glass vessels and connected together by a rubber tube full of the solution. The electrode containers could be raised and lowered at will, permitting a difference in level of 377 cm.

The following table gives a summary of his results, including a comparison between the value T_a for the transference number of the anion as calculated from his results and as determined by the Hittorf method. The measurements were made with calomel electrodes (in the case of CdCl_2 with Cd amalgam electrodes as well). The e.m.f. is expressed in microvolts per centimeter difference in height.

Salt.	% Conc.	e. m. f.	T_a	T_a Hittorf
KCl	16.8	+0.0510	0.50	0.52
NaCl	19.9	-0.0315	0.66	0.65
LiCl	17.3	-0.109	0.77	0.75
HCl	3.56	-0.0218	0.150	0.175
BaCl ₂	17.0	+0.170	0.64	0.65
CdCl ₂ (Cal. Elect.)	30.1	-0.183	1.10	} 0.82
CdCl ₂ (Amalg. Elect.)	30.1	-0.221	1.02	

Des Coudres estimates that the uncertainty in the values of the electromotive forces given is not greater than ± 0.009 microvolts.

In the present investigation, a new attempt was made to increase the accuracy of this method of determining transference numbers, by substituting for the effect of gravity the force produced by a centrifugal machine of considerable power. As will be seen in the sequel, the average deviation between successive measurements has in this way been reduced to a very small amount. An estimation of the actual error in the results is, however, somewhat difficult to make.

2. DERIVATION OF AN EXPRESSION FOR THE ELECTROMOTIVE FORCE.

In order to derive an expression for the electromotive force produced in an electrolytic solution by the action of gravity, let us consider a vertical tube of height h , filled with the solution and provided with electrodes at the top and bottom. If E is the potential difference in volts between the upper and lower electrodes produced by the action of gravity, then by allowing one faraday of electricity to flow under this electromotive force we could obtain the external work $10^7 EF$ ergs. The passage of this electricity through the solution is accompanied, however, by the transfer of a certain net weight of material from the upper electrode to the lower one. From the principles of energetics, it is evident that this external energy $10^7 EF$ which we could obtain will just be sufficient to restore the solution to its original condition, that is, will do the work of raising the transferred material back from the lower electrode to the upper one. For the sake of definiteness, let us suppose that the electrolyte is a solution of an iodide ($C^+ I^-$) and that we are using iodine electrodes, consisting in practice of platinum electrodes with a small amount of iodine dissolved in the solution. If, now, we let one faraday of electricity flow through the solution, we know from the experiments of Faraday and of Hittorf that one atomic weight of iodine or M_I grams will be liberated at the anode or upper electrode and will disappear from the lower electrode, and at the same time that there will be a change in the ratio of salt to water at the two electrodes such that $T_c M_c$ gms. of salt will have apparently been transferred from the anode to the cathode, where T_c is the ordinary or Hittorf transference number of the cation and M_c is the molecular weight of the salt. In order, therefore, to restore the solution to its original condition of uniform concentration, it is necessary to raise $T_c M_c$ gms. of salt from the lower electrode to the upper one at the same time lowering one atomic weight of iodine. If we raise and lower these substances *through* the solution it is evident that they will be buoyed up by force equal to the weight of the volume of solution which they displace. Hence if g is the acceleration due to

gravity, and d the density of the solution, the downward forces acting respectively on the salt and the iodine will be $g T_s M_s (1 - v_s d)$ and $g M_I (1 - v_I d)$ where v_s and v_I are the "partial" specific volumes⁴ of the substances. Equating the external electrical work to the work done against these forces in transferring the substance from one electrode to the other, we have the desired relation⁵

$$10^7 EF = hg [T_s M_s (1 - v_s d) - M_I (1 - v_I d)]. \quad (1)$$

If instead of using a gravity cell we should rotate our solution n times per second, with electrodes at r_1 and r_2 , since the centrifugal force acting on one gram at any radius r is $4\pi^2 n^2 r$, the work done in carrying one gram from r_2 to r_1 would evidently be

$$\int_{r_1}^{r_2} 4\pi^2 n^2 r dr = 2\pi^2 n^2 (r_2^2 - r_1^2) \quad (2)$$

and our equation for electromotive force becomes

$$10^7 EF = 2\pi^2 n^2 (r_2^2 - r_1^2) [T_s M_s (1 - v_s d) - M_I (1 - v_I d)]. \quad (2)$$

We see that the value of the electromotive force which is to be measured is proportional to the factor hg or $2\pi^2 n^2 (r_2^2 - r_1^2)$. In the experiments of Des Coudres on gravitational cells, the factor hg was 360,000, while with his rotating apparatus the value of the corresponding factor was 583,000. In the centrifugal experiments which are to be described in this paper the value of the factor was raised to 114,000,000.

The Effect of Hydration.

It has been shown by the careful researches of Buchböck⁷ and especially of Washburn⁸ that it is possible to distinguish between the ordinary Hittorf transference number and the so-called "true" transference number in which the motion of the ions is referred to a non-

⁴ For a definition of "partial" volumes, see page 131.

⁵ In order to derive this equation, any reversible method might be used for restoring the solution to its original condition of uniform concentration. For example, the apparent difficulty of moving the substances *through* the solution can be obviated by removing them from the solution with the help of semi-permeable membranes. It is easy to show, however, that the relation derived is the same.

⁶ It may also be pointed out that the expression $2\pi^2 n^2 (r_2^2 - r_1^2)$ is the increase in kinetic energy when one gram of material is transferred from r_1 to r_2 .

⁷ Buchböck, Z. physik. Chem. **55**, 563 (1906).

⁸ Washburn, Tech. Quart. **21**, 164 (1908), Journ. Amer. Chem. Soc. **31**, 322 (1909).

electrolytic indicator dissolved in the solution instead of to the water. If water is carried by the current, owing to hydration of the ions, then the two transference numbers will be different.

The Hittorf transference number gives, however, the actual number of equivalents of salt which apparently disappear in the neighborhood of one electrode and appear at the other when one faraday of electricity is sent through the solution, and hence the Hittorf transference number gives us the amount of salt which must be moved in order to restore the solution to its original condition of uniform concentration. From a consideration of the method by which the equation for the electromotive force was derived, it is obvious that the *Hittorf* transference number is the one which has been determined in this research.

3. KINETIC DERIVATION OF THE ELECTROMOTIVE FORCE EXPRESSION.

In order to derive the equations used in this article, we have considered the production of the electromotive force in a rotating solution from a thermodynamic standpoint. The fact that more work was needed to send a current through a salt solution from the outer to the inner electrodes than in the reverse direction, could be predicted from thermodynamic principles, and the electromotive force, corresponding to this work, could be calculated merely from a knowledge of certain properties of the solution such as transference number and density, which can be experimentally determined. It is also instructive, however, to look at the question from a "kinetic" or molecular point of view. The fact that an electromotive force *is spontaneously* produced by centrifugal force gives us a real knowledge of the internal structure of an electrolytic conductor. It is, indeed, the most striking proof of the existence of free ions in an electrolyte.

Considered from a "kinetic" point of view, a solution of potassium iodide contains free potassium ions and free iodide ions. The iodide ions, however, corresponding to their greater atomic weight, are much denser than the potassium ions, and hence when the solution is rotated they move more readily towards the outer portion of the solution and charge it negatively. In fact from a consideration of the forces acting on the ions in the solution, it is possible to derive the same equation for the electromotive force of a gravity cell as that already obtained from thermodynamic reasoning. The method of proof is similar to that used by Nernst in his consideration of the diffusion cell.

Consider an iodide (C^+I^-) of molecular weight M_i dissociating into the ions C^+ and I^- of atomic weights M_c and M_i . Let v_s be the partial specific volume of the salt in solution and v_c and v_i be the same

quantities for the positive and negative ions respectively. Now let us subject a solution of this salt to the action of gravity. If the positive ion C^+ is denser than the iodide ion, it will tend to move downward through the solution more rapidly and will produce a potential gradient in the solution $-dE_1/dh$. As this potential gradient is produced, however, it tends to decrease the downward velocity of the positive ion and increase the velocity of the negative ion so that under the final potential gradient produced they will move downward through the solution with equal velocities. We may now proceed to derive expressions for these equal velocities.

The total downward force acting on one mol of positive ions is the weight (gM_c), minus the buoyant force exerted by the solution ($gM_c v_c d$), minus the electrical repulsion ($10^7 F dE_1/dh$) corresponding to the potential gradient. If u and v are the velocities with which the positive and negative ions move under unit force, the velocity with which they will move under the actual forces can now be calculated by simple multiplication, since the validity of Ohms law in solutions shows us that the velocity with which the ions move is proportional to the force acting on them.

Equating the velocities of the negative and positive ions, we have⁹

$$u \left(gM_c (1 - v_c d) - 10^7 F \frac{dE_1}{dh} \right) = v \left(gM_I (1 - v_I d) + 10^7 F \frac{dE_1}{dh} \right).$$

Solving for dE_1/dh and integrating between the limits o and h , where h is the difference in height between the electrodes, we have

$$10^7 E_1 F = hg \left[\frac{u}{u+v} M_c (1 - v_c d) - \left(1 - \frac{u}{u+v} \right) M_I (1 - v_I d) \right]. \quad (3)$$

In order to obtain the actual electromotive force between the electrodes, we must consider not only the potential gradient in the solution, but also the potential drops which occur directly at the electrodes due to the electrode reaction $\frac{1}{2} I_2 + \Theta = I$. Since this reaction is accompanied by the change in volume $M_I (v_I - v_{I_2})$ and takes place under the difference in pressure between the upper and lower electrodes which is

⁹ It should be noted that when the concentration of the salt in the lower portion of the tube has appreciably increased, the concentration gradient adds new forces tending to slacken the downward motion of the ions. When the final equilibrium is reached the concentration gradient will be such that no potential gradient exists. We are interested, however, in the original condition before appreciable concentration changes have taken place.

equal to hgd , we must add to the electromotive force E_1 as given in equation (3), the electromotive force E_2 given by the equation below, which is derived by equating the external electrical work to the work produced by the change in volume

$$10^7 E_2 F = M_I (v_I - v_{I_2}) hgd.$$

Noticing that

$$\frac{u}{u+v} = T_c$$

we obtain

$$10^7 (E_1 + E_2) F = hg [T_c M_c (1 - v_c d) + T_c M_I (1 - v_I d) - M_I (1 - v_{I_2} d)]$$

$$\text{or} \quad 10^7 EF = hg [T_c M_s (1 - v_s d) - M_I (1 - v_{I_2} d)],$$

which is the same equation we originally obtained by thermodynamic reasoning.

The real interest attached to this kinetic consideration is the almost absolute proof it offers that some degree of dissociation or at least polarization of the salt molecules exists in aqueous solutions. Since unless the positive and negative components of the salt can move relative to one another we cannot see how a potential gradient is set up by centrifugal separation. The method gives, of course, no idea of the magnitude of the degree of ionization.

4. DESCRIPTION OF APPARATUS.

The general arrangement of the rotating apparatus is shown in Figure 1. It consists of a steam turbine A, with vertical shaft, driving the rotator B, which contains the tubes of solution. Electrical connection with the electrodes in the solution was made through the mercury contacts C.

The Steam Turbine.

The turbine used was a thirty horse-power de Laval loaned for this investigation by the General Electric Co. The turbine wheel was ten inches in diameter. A 2-inch steam pipe D leads into the annular space E from which the nozzles lead up to the turbine wheel. The holes F are opposite the openings to the nozzles and are threaded to receive the bonnets of the nozzle valves (not shown in the drawing). A 3-inch exhaust pipe leads from the exhaust chamber G, on the side away from that shown in the drawing. The turbine is supported on the legs H, bolted to the cross beams I. It is also bolted to the block J. Largely for the sake of safety, the apparatus was re-designed

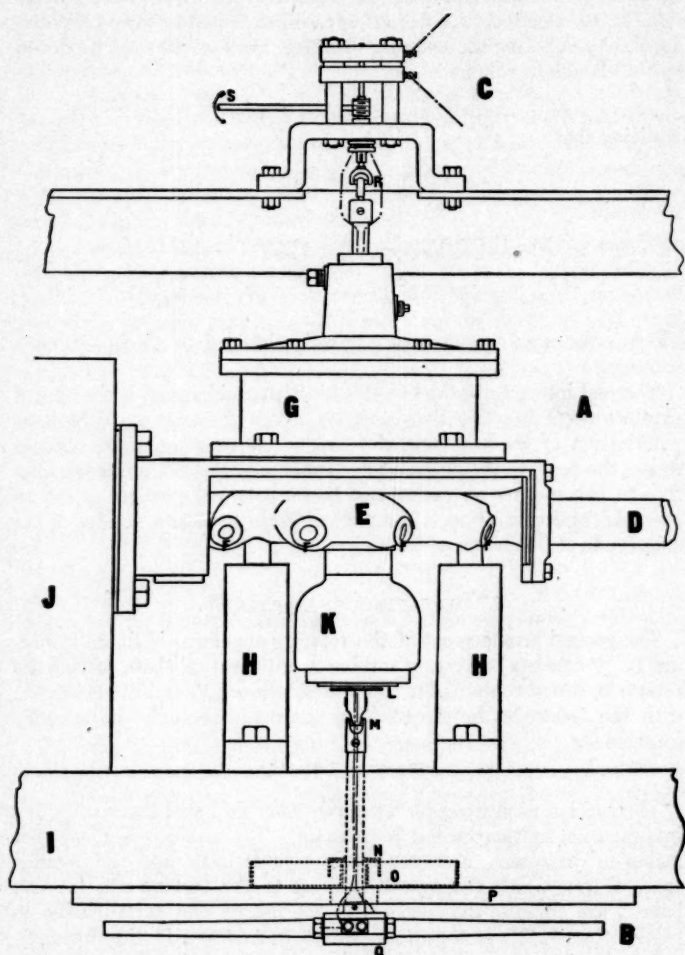


FIGURE 1. General Arrangement of the Rotating Apparatus. $\frac{1}{2}$ size.

with a vertical shaft and was placed in a specially constructed pit. The vertical shaft necessitated the design of some form of thrust bearing to support the rotating system.

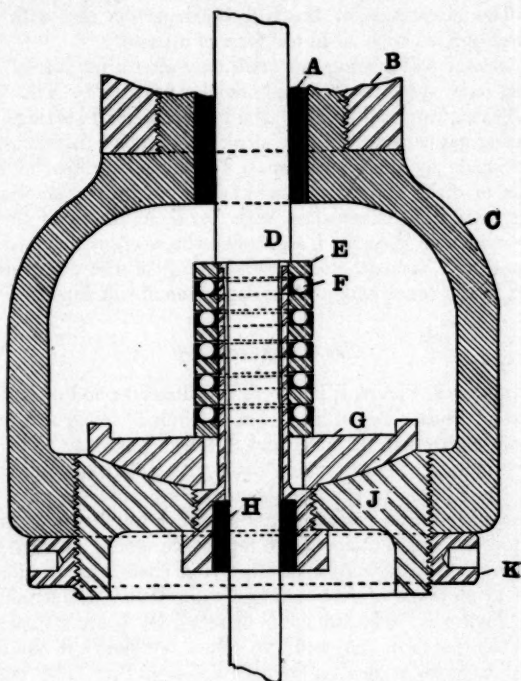


FIGURE 2. The Thrust Bearing. $\frac{1}{2}$ size.

The Thrust Bearing.

The thrust bearing used was contained in the case K, Figure 1. The details are shown in Figure 2. It consists of a series of five ball bearings, placed one above the other, so as to distribute the total relative motion which must be cared for. Each ball bearing consists of a series of balls F, in a brass cage, between two hardened steel washers. A shoulder on the shaft D rests on the topmost washer E, and the lowest bearing rests on the levelling washer G, which has a spherical

seat. The nut K locks the adjustment of the bearing at the proper height. The lateral bearings A and H as well as the top bearing of the turbine itself, consist of eminently satisfactory graphite-lined bushings supplied by the Graphite Lubricating Co., Bound Brook, N. J. The lubrication of the ball bearings was also with graphite which was applied with oil in the form of a paste.

This form of ball bearing was tried only after a number of bearings, including one specially designed for the purpose by The Standard Roller Bearing Co., had failed. The individual ball bearings of which this bearing was constructed were stock 13/16 inch "ball thrust collar" bearings made by the above firm. The ingenious idea of replacing the series of disks sometimes used in step bearings by a series of ball bearings came in a conversation with Dr. C. A. Kraus of this laboratory, to whom, in general, I am under the deepest obligation for an intelligent and sympathetic understanding of the many difficulties involved in the construction of an apparatus of this kind.

The "Spinning Top."

The rotator B, Figure 1, is two feet in diameter and consists of two hollow steel arms, screwed into a central hub P. The rotator is hung on a shaft 13/16 inch diameter and 8-1/2 inches long. This shaft is flexibly connected to the turbine shaft with a Hooke joint M, which permits the rotator to revolve about its own center of gravity. The arrangement is in the nature of a "spinning top." In order to prevent a precessional motion of the top which would quickly raise the rotator shaft to a horizontal position, the shaft was steadied at the point N by a system of cords not shown in Figure 1, but indicated in plan in Figure 3. The two cords MN and OP prevent motion of the shaft in the direction AA, and two others not shown in the figure are arranged to prevent motion in the direction BB. The cords were drawn tight against the shaft through the stationary supports at W, X, Y, and Z. The cords were braided cotton 5/32 inch in diameter and the wear on them, strange as it may seem, was very inconsiderable. This arrangement of cords was adopted after experimenting with many forms of steadying bearing, in which it was attempted to prevent the precessional motion with rubber washers, springs, or pneumatic dash pots.

This plan of driving the rotator as a spinning top must be considered as one of the distinctive features of the apparatus. By this means the rotator was driven up to a speed of 7850 revolutions per minute, giving a rim speed of nearly 50,000 feet per minute. At this

speed there was a certain amount of vibration of the steadying cords. In general, however, it was found possible to raise the speed at which this vibration took place by moving the supports W, X, Y, and Z nearer to the shaft, and there is no doubt that the apparatus could be arranged to go to still higher speeds. As will be seen later, for other reasons, the actual measurements had to be made at speeds of 5000 revolutions or less.

The fact to be specially noticed with regard to this "spinning-top method" is that it permits the driving at a very high speed of a rotator which has not been specially adjusted for either "stationary" or "running" balance.

The method was adopted after considerable experimenting with a rotator driven on a shaft with fixed bearings. Although this rotator had been put into "stationary" balance, it caused so great a vibration that one of the bearings gave way at a speed under 2000 revolutions per minute, wrecking a machine upon which a considerable amount of labor had been expended.

The mathematical theory of a symmetrical top rotating with one fixed point and acted upon by gravity alone has been completely developed. It has further been shown by H. Lamb¹⁰ that, in the case of a rotating top hanging below its fixed point, as in this apparatus, the effect of *viscous forces* in the Hooke joint is to produce a gradually increasing precessional motion which would finally raise the axis of the top horizontal. This is the precessional motion which was prevented by the steadying device described above. It must be noticed in general, in designing rotating apparatus of this kind, that the actual motion may differ considerably from that pre-

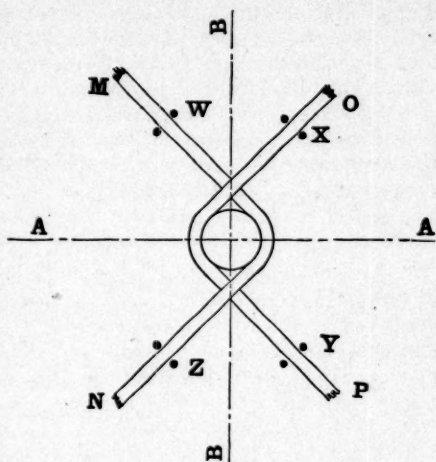


FIGURE 3. The Steadying Cords.

¹⁰ H. Lamb, Proc. Roy. Soc., 80, A 168 (1908).

dicted by the dynamical equations since, among other things for example, the latter take no account of restraining forces such as were introduced in this case by the steadying cords.

Some experiments, on a small scale, were made with rotating tops, driven through a Hooke joint from below. There were indications that this would be a most satisfactory method of driving an unbalanced rotor. The whole field is a very profitable one for research.

As a practical detail, it should be pointed out that the rotator shaft must be made short enough not to reach its own period of vibration at the speed employed. It was found impracticable to run this rotator with a shaft 22 inches long.

The Rotator.

Fig. 4 gives a detail of one of the two arms which screw into the central hub of the rotator. These arms were made from seamless steel tubing bored out to one-half inch inside diameter. The peripheral end of the tube was closed by screwing in a plug of steel, the threads of which were figured to withstand the shear at 8000 revolutions per minute, produced by the combined outward action of the centrifugal force of the plug and that of the contents of the tube, assuming them to be a liquid of specific gravity 1.3. In order to prevent leakage of liquid through the screw threads, the plug was silver soldered in position.

The thickness of wall at the peripheral end of the tube was enough to prevent bursting as calculated by Clavarino's formula for thick hollow cylinders. This thickness of wall was also great enough to sustain the outward tension as far as the point B, 3 inches from the end of the tube. From this point on towards the center the tube had to gradually increase in diameter in order to sustain the constantly increasing load. If r is the radius at any point where the section is s , D the density, f the tensile strength of the material, and n the number of revolutions, evidently $f ds = 4\pi^2 n^2 r D s dr$. Integrating this equation and solving, the proper dimensions for the inner end of the arm were found. The screw thread on the inner end of the arm was sufficient to prevent the arm from shearing out from the hub.

The Solution Tube.

The solutions experimented on were iodides with iodine electrodes. The actual tubes which contained the solutions were made of glass. This was the only material found which was an insulator and at the same time was not attacked by the iodine. The latter condition was

of great importance since the slightest loss of iodine in the neighborhood of either of the electrodes created a large potential difference between them. The tubes were carefully annealed and were floated in oil inside the rotator arms; nevertheless, the end thrust produced by the centrifugal force was great enough to break many tubes even at speeds as low as five thousand revolutions per minute.

With the hope of obtaining some material which would stand higher speeds, a great many other materials for tubes were investigated, including porcelain, paraffined paper and wood, celluloid, vulcanite, and steel tubes lined with paraffine, sulphur, and enamel but none was found

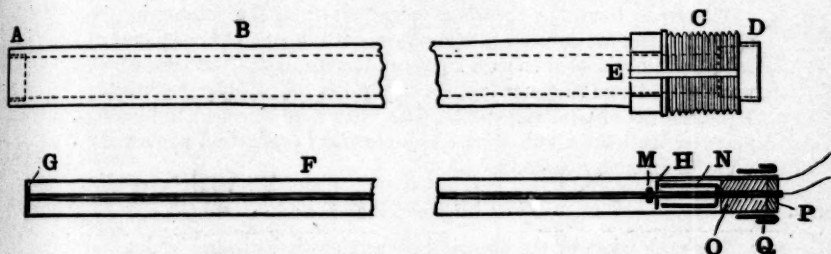


FIGURE 4. Rotator Arm and Solution Tube. $\frac{1}{2}$ size.

satisfactory. Tubes of vulcanite, which has a specific gravity only slightly greater than water, practically floated in the steel arm without danger of breakage, and many experiments were made with them. There seemed, however, to be a distribution of iodine between the hard rubber and the solution which made it very difficult to keep the iodine concentration the same at the two electrodes, and they were finally discarded in favor of glass.

Figure 4 gives a detail of one of the tubes with its electrodes. The tubes were annealed by carefully wrapping them in asbestos and heating in a large electric furnace to about 500°C . and then allowing the furnace to cool, which took a day and a half. The electrodes were platinum. The outside electrode G rested on the bottom of the tube. The connecting wire had to be platinum-iridium in order to stand the centrifugal force. This wire was insulated from the solution by a glass tube which is slightly enlarged at M. On the enlargement M rests the inner electrode H. N shows the cross section of a glass thimble which is slipped down on to the electrode. A bubble of air was entrained in this thimble to allow for temperature expansion, and to provide a means of stirring the solution. Melted ceresin which had

been specially purified was poured on top of the thimble at O and this was covered by a thin layer of a molten cement P which consisted of a mixture of wood tar and shellac.¹¹

The tube is made to slip into the rotator arm and rests at the outside end on a disk of rubber packing. It is surrounded by oil to equalize the hydrostatic pressure. A short piece of rubber tubing is slipped onto the glass tube and turned back on itself as shown in the figure at Q. The tube projects from the end of the arm far enough so that the turned-back rubber just meets the end of the arm at D, and a piece of "bill-tie" tubing is slipped over the rubber tubing and the arm to prevent leakage of oil.

The leads from the electrodes come out from the rotator in the grooves E and are covered with small rubber tubing. Ordinary optical tubing was not a good enough insulator, but insulation was used which was stripped from 22-gauge rubber-covered wire supplied by the Simplex Electrical Co. of Cambridgeport. The wires were attached to binding posts on the rotator hub, from which electrical connection was carried up to the mercury contacts.

The Electrical Connections.

The path taken by the electrical connections is indicated by dot and dash lines in Figure 1. Leads from the binding posts on the rotator hub pass up through the center of the hollow rotator and turbine shafts and make connection with the mercury contacts. The wire used was 22-gauge rubber covered, as ordinary insulation would not stand the severe conditions of temperature and the effect of moisture.

At L in Figure 1 is a brass disk about 2-1/2 inches in diameter fastened to the rotating shaft. This disk prevents any leakage of water from the turbine trickling down the Hooke joint and getting into the hollow rotator shaft and thus interfering with the insulation. O is a stationary pan about 10 inches in diameter with a central hole for the shaft to pass through. This pan catches accidental dripping from the turbine and protects the hub of the rotator and its binding posts. Further protection is provided by a copper disk N with turned-down edges. This disk rotates with the shaft and covers the central hole in the pan O. The disk also radiated the heat from the turbine and from the friction of the steadying cords, which otherwise traveled down the shaft and produced bad temperature differences between the central and peripheral electrodes.

¹¹ This useful cement was discovered by Dr. C. A. Kraus and Mr. R. D. Mailey of this laboratory.

The Mercury Contacts.

Connection between the leads, which came up through the hollow shafts, and the external measuring circuit was made through the mercury contacts C indicated in Figure 1 and shown in detail in Figure 5. The leads from the electrodes were made fast to the binding posts M and N, and electric connection was made through the small rotating

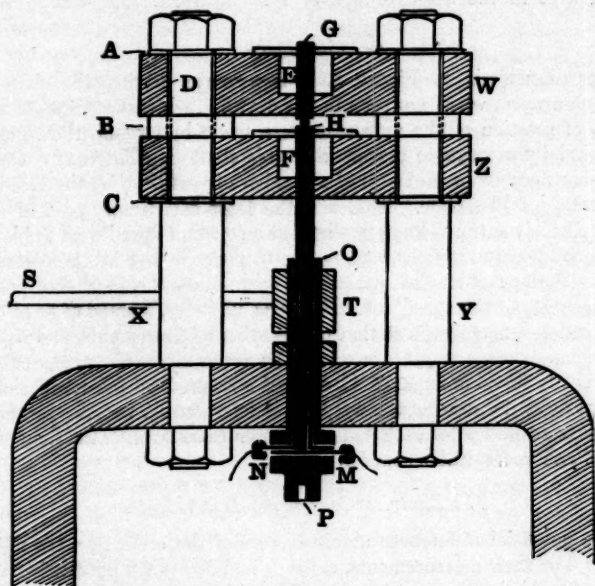


FIGURE 5. The Mercury Contacts. $\frac{1}{2}$ size.

shafts G and H with mercury, which was placed in the circular troughs E and F in the steel blocks W and Z. The two small shafts are insulated from one another and from the outside driving shaft O by fine rubber tubing, and at the bottom by vulcanite disks. The steel blocks are insulated from each other and their supports X and Y by vulcanite washers and sleeves. Connection is made from the steel blocks to the measuring instruments.

The apparatus was specially designed with the purpose of eliminating the production of electromotive forces at the point of contact

between the moving and stationary parts. For this reason, the shafts were made as small as possible, $3/16$ inches in diameter, thus reducing the relative velocity at the point of contact, mercury was chosen as the contact substance, and the whole apparatus was made of the same material, steel, throughout. Measurements of the electromotive forces occurring in these mercury contacts, were made by driving the apparatus with the contacts short circuited. The potential differences found were in the neighborhood of $1/20$ millivolt.

The Magneto.

Returning again to Figure 5, T is a worm driving the shaft S through a worm wheel not seen in the drawing. Measurements of the speed of rotation of the apparatus were made by reading the voltage produced by a magneto driven from this shaft S. This was a small three-bar magneto manufactured a number of years ago by the Holtzer Cabot Co. of Brookline. This was the least satisfactory part of the apparatus, since the voltage readings at a constant speed were liable to small, sudden fluctuations largely due to poor contact at the commutator. Both graphite and woven wire commutator brushes were tried. The accuracy of the speed determinations, however, seemed to be of the same order of magnitude as that of the other measurements, and it did not seem advisable to procure one of the newer magnetos or any of the more costly forms of apparatus for speed measurement. A small motor was arranged for driving the magneto independently, and the magneto was standardized after each series of measurements with the help of a stop watch and suitable counter.

The Electrical Measuring Instruments.

The potential differences obtained were of the order of a few millivolts. For their measurements, a Leeds and Northrup potentiometer and a suitable galvanometer were used. A cadmium element supplied by the Weston Electric Co. was used as a standard cell, and this was further compared with another Weston cell both at the beginning and end of the measurements. In the actual experiments a reading of the voltmeter which gave the speed of the apparatus, and the potentiometer reading were taken as nearly simultaneously as possible.

5. THE METHOD OF PROCEDURE.

With the apparatus described, measurements were made on solutions of potassium, sodium, lithium, and hydrogen iodides. The solutions contained exactly 1 mol of the salt and $1/100$ mol of I_2 in a kilogram

of water. In the case of hydrogen iodide, owing to the oxidation of the acid, there was a gradual increase in the amount of I_2 present in the solution. A rough colorimetric analysis of the solution as finally used showed the presence of about 2/100 mol I_2 per kilogram of water.

The glass tubes which contained the rotating solutions have already been described. In the experiments as finally performed only one tube was used, an approximate counterbalance being placed in the other arm of the rotator. By connecting two tubes in series, it would have been possible to double the electromotive force to be measured. This would not have greatly increased the certainty of the measurements, however, since, on stopping the rotator, the residual potential differences between the two electrodes were always found to be in the same direction, and by connecting two tubes in series the size of the error as well as that of the potential difference to be measured would have been increased.

Before filling the tubes, they were carefully rinsed with some of the solution to be used. The electrodes were heated to incandescence in a blast lamp and placed in the solution without being touched by the fingers.¹² By using care, it is possible in this way to reduce the original electromotive force between the two electrodes to the neighborhood of 0.2 millivolt or less. The small variable electromotive forces which do persist are probably partly due to differences in temperature between the two ends of the solution. As already described the tubes were sealed with purified ceresin. This was almost the only material found whose presence near one of the electrodes did not produce a large electromotive force.

After the apparatus had been set up ready for rotation it was tested for insulation. This is very important, since any leakage between the leads coming from the solution would apparently have decreased the size of the electromotive force produced. The test was carried out by disconnecting one of the leads from its binding post on the hub of the rotator and applying a drop of $1\frac{1}{2}$ volts at the other end of the leads where they joined the measuring system. A galvanometer was in series with the potential drop to measure the current leaking from one lead to the other.¹³

In general, for the final experiments the galvanometer was absolutely stationary, and if there was more than a trace of a deflection, the

¹² Laurie, *Zeits. f. phys. Chem.* **64**, 617 (1908).

¹³ In order to make the test more thorough the lead which had been disconnected from the binding post was connected to the steel rotator. Until considerable experience had been gained, it was very difficult to eliminate leaks between the wires coming from the electrodes and the rotator.

trouble was eliminated before making a run. A deflection of one millimeter on the galvanometer scale would have corresponded to a resistance of about 1.5×10^9 ohms between the leads.

In the experiments a number of readings of the residual electromotive force were taken with the rotator stationary. It was then brought up to speed and a new series of readings commenced as soon as possible. After running for several minutes, the steam was shut off and more readings of the residual electromotive force commenced as soon as the rotator had stopped. The voltmeter attached to the magneto was placed near the potentiometer so that a determination of the speed of the apparatus was made immediately after each measurement. The approximate time when each measurement was taken was also recorded.

At the end of a day's measurements, the magneto was standardized with a stop watch and counter. Usually, about a half a dozen standardizing runs were made at speeds in the neighborhood of those used in the actual measurements. Each run lasted about a minute. The stop watch was started when some even figure appeared on the counter, and stopped similarly about a minute later. In general, five readings of the voltmeter were made, one before the stop watch was started, the next three at intervals of fifteen seconds, and the last one after the watch had been stopped. It was not easy to hold the speeds constant enough to make standardizing runs of over a minute desirable.

6. THE EXPERIMENTAL RESULTS.

In the following tables are given the data on which the calculations for each of the salts investigated are based. The first column gives the time when the observation was taken, the second column, the reading of the voltmeter, V (in decivolts), which indicated the speed of the apparatus, and the third column, the potential difference in millivolts, $E \times 10^3$, this being called negative when in the opposite direction from that produced by the centrifugal force. The radii of the two electrodes r_2 and r_1 are also given, and the data for the standardization of the magneto. In the case of all salts investigated, the inside electrode was positive with respect to the outside one during rotation.

It is a striking fact that, upon stopping the rotator the residual electromotive force is always found to be in the opposite direction from that produced by the centrifugal force. It will also be seen from an examination of the data that there is a general tendency for this residual electromotive force to increase somewhat in magnitude and then in the course of a few minutes gradually to disappear. The average

magnitude reached by this residual electromotive force is 0.2 to 0.3 millivolts.

At first sight, it might seem possible to explain this residual potential difference by assuming that the outer electrode was heated more by the friction of the air, during rotation, than the inner one; since as a matter of fact, a difference in temperature of $1^{\circ} C.$ would have produced a residual electromotive force of about 0.25 millivolts in the direction actually found.¹⁴ This explanation, however, would not account for the fact that the residual electromotive force tends to increase after the machine has been stopped, and the very conditions removed which were supposed to create the temperature difference.¹⁵ This increase in the magnitude of the residual electromotive force after stopping the machine was much easier to follow and the final value reached was much larger, in some earlier experiments where *vulcanite* tubes were used instead of glass for containing the solution.¹⁶ This might indicate that the gradual increase of electromotive force after stopping the rotation is due to the gradual emergence into the solution of some constituent which had been forced into the pores of the tube by the centrifugal force or the pressure. Whatever the true explanation, the phenomenon is so complicated that it seemed best not to hazard a guess as to the probable size of the residual electro-

¹⁴ In order to determine the value of the electromotive forces produced by temperature differences between the electrodes, the thermoelectric power was carefully measured for a number of different circuits of the type, — platinum → salt solution: salt solution → platinum. The writer hopes to present the results of measurements of this kind in a later paper.

¹⁵ Attempts were made to actually measure the temperature difference between the two electrodes, by placing in the tube an ordinary thermoelectric circuit with iron-nickel junctions at the outer and inner ends. Connection between this thermoelectric circuit and the measuring instruments was made through the mercury contacts already described. It was found, however, that the small electromotive forces arising in these mercury contacts were large enough to obscure those produced by the iron-nickel junctions, and the method was abandoned. There seem to be no practical metallic junctions of higher thermoelectric power than the iron-nickel combination.

In some earlier experiments very definite temperature effects were produced by heat which traveled down the rotator shaft. These effects were eliminated, however, by the copper radiating disk N, Fig. 5, already described, see p. 124.

¹⁶ In these experiments made with vulcanite tubes, there was also the difference that the rotator was driven in a closed case instead of in the open air. Since the air in the case was considerably heated by the rotation, larger temperature differences might have been expected between the two electrodes. Nevertheless, this would not account at all for the increase in residual electromotive force after the rotator had been brought to rest.

motive force *during* rotation and no correction was made for it in the calculations

Further development of the centrifugal method should be in the direction of eliminating these residual potential differences between the electrodes. This could best be done by having the liquid circulate through the apparatus so as to pass from one electrode to the other and thus assure the same conditions at both.

TABLE I.

(Dec. 2, 1909.)

Solution: Molal KI, $\frac{1}{100}$ Molal I₂.

$r_2 = 29.40$ cm., $r_1 = 4.3$ cm.

Standardization of magneto: $-\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 1.050$ (7 expts.
av. dev. ± 0.0145).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 1.050$ = rev. per sec.	$\frac{E}{n^2} \times 10^6$.	Dev. from mean.
10.54	0	-0.30
11.12	0	-0.10
.23	0	-0.50
.25	0	-0.55
.28	60.0	+2.58	62.9	652	- 5
.29	58.5	2.47	61.4	655	- 2
.30	59.0	2.52	61.9	658	+ 1
.30½	59.8	2.55	62.8	647	-10
.31½	0	-0.15
.32	0	-0.30
.34	0	-0.18
.36	0	-0.14
.40	0	-0.17
.41½	71.5	+3.65	75.0	649	- 8
.42	71.2	3.73	74.7	668	-11
.43½	72.0	3.73	75.5	655	- 2
.44	72.7	3.90	76.2	672	+15
.45	73.1	3.93	76.7	668	+11
.46	0	-0.25
.47	0	-0.18
.49	0	+0.05
.50½	0	0.17
.52½	0	0.25
.55	78.0	4.38	81.9	653	- 4
.55½	77.5	4.35	81.3	658	+ 1
.56	77.0	4.25	80.8	651	- 6
.57	...	4.25
Average				657.1	± 6.3

7. RATIO OF THE ELECTROMOTIVE FORCE TO THE SQUARE OF THE NUMBER OF REVOLUTIONS PER SECOND.

From equation (2) it is evident that the electromotive force produced by the rotation should increase as the square of the number of revolutions per second, that is, E/n^2 for a given solution should be a constant. The degree of the constancy of this quantity is illustrated by the fifth column in Tables I-IV which gives the values of E/n^2 as calculated from the data. Considering the separate runs in a series of measurements, we see a tendency for the individual measurements of the *first* run to show the largest deviations from the mean. There is probably some connection between this and the fact that the value reached by the residual electromotive force is also largest after the first run in a series. In many of the individual runs there is a tendency for the electromotive force to decrease somewhat during the run. This would correspond to the gradual production of a negative residual electromotive force. As already pointed out, the nature of these residual potential differences is too uncertain to permit of a trustworthy correction.

8. THE PARTIAL VOLUMES OF IODINE AND THE IODIDES.

Before making a calculation of the transference numbers from the electromotive force data which we have just considered, a knowledge of the partial volumes of iodine in iodide solutions and of the iodides in aqueous solution is necessary.

The partial specific volume of any constituent of a solution may be defined as the increase in volume of the solution when one gram of the constituent in question is added to a quantity of the solution so large that the addition causes no appreciable change in concentration. In the language of mathematics, if the addition of Δm grams of the constituent at the concentration under consideration produces an increase of Δv cc. in the volume of the solution, the partial volume of the substance may be defined as the limit approached by $\Delta v/\Delta m$ as Δm approaches zero.

The quantity $\Delta v/\Delta m$ and its limit the partial volume dv/dm may be obtained by the same experimental methods used for the determination of the specific gravity of solutions or, indeed, may be calculated from specific gravity data if such are available.

The purpose of this section is to show the method of calculating partial volumes from picnometer weighings or from specific gravity data and also to present the results of some experimental determinations of the partial volume of iodine in potassium iodide solution as well as the

TABLE II.

(Dec. 23, 1909.)

Solution: Molal NaI, $\frac{1}{100}$ molal I_2 . $r_2 = 29.45$ cm., $r_1 = 4.2$ cm.Standardization of Magneto:
$$-\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 0.8695 \text{ (8 exp.}$$
av. dev. $\pm .0035$).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8695$ = rev. per sec.	$\frac{E}{n^2} \times 10^6$.	Dev. from mean.
10.12	0	-0.16
.15	0	-0.04
.22	0	-0.35
.25 $\frac{1}{2}$	66.2	+3.00	57.6	904	+15
.26 $\frac{1}{2}$	65.9	2.95	57.3	898	+9
.27	65.9	2.83	57.3	862	-27
.28	65.9	2.83	57.3	862	-27
.28 $\frac{1}{2}$	66.2	2.92	57.6	880	-9
.30	0	-0.24
.30 $\frac{1}{2}$	0	-0.28
.31 $\frac{1}{2}$	0	-0.17
.32 $\frac{1}{2}$	0	0.00
.35	73.2	+3.61	63.7	889	0
.35 $\frac{1}{2}$	74.2	3.70	64.5	889	0
.36 $\frac{1}{2}$	74.8	3.75	65.1	885	-4
.37	75.1	3.79	65.3	888	-1
.38	76.0	3.88	66.1	887	-2
.39 $\frac{1}{2}$	0	-0.26
.40	0	-0.26
.41	0	-0.17
.42	0	-0.07
.43 $\frac{1}{2}$	0	-0.00
.45	0	+0.03
.46	0	0.05
.48 $\frac{1}{2}$	74.5	3.70	64.8	881	-8
.49	74.2	3.72	64.5	893	+4
.50	74.8	3.72	65.1	877	-12
.50 $\frac{1}{2}$	74.5	3.71	64.8	883	-6
.51	74.5	3.70	64.8	881	-8
.52	74.0	3.66	64.4	882	-7
.53 $\frac{1}{2}$	0	-0.15
.54 $\frac{1}{2}$	0	-0.10
.55 $\frac{1}{2}$	0	-0.06
.57	0	-0.05
.58 $\frac{1}{2}$	0	-0.06
.60 $\frac{1}{2}$	0	-0.10
11.03	80.0	+4.37	69.5	905	+16
.03 $\frac{1}{2}$	81.2	4.53	70.6	910	+21
.04 $\frac{1}{2}$	82.8	4.60	72.0	888	-1
.05	83.2	4.65	72.3	889	0
.06	84.0	4.77	73.0	895	+6

TABLE II. — Continued.

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8695$ = rev. per sec.	$\frac{E}{n^2} \times 10.6$	Dev. from mean.
.06½	84.1	4.80	73.1	899	+ 10
.07½	0	-0.23
.08	0	-0.23
.10	0	-0.04
.11½	0	+0.12
.14	0	0.17
.16	0	0.17
.18½	74.1	3.73	64.5	897	+ 8
.19½	75.0	3.85	65.2	905	+16
.20	74.8	3.76	65.1	887	- 2
.20½	74.2	3.73	64.5	896	+ 7
.21½	73.9	3.68	64.2	892	+ 3
.22½	0	-0.24
.23½	0	-0.18
.28	0	+0.18
Average				889.0	±8.5

partial volumes of potassium, sodium, lithium, and hydrogen iodides in molal solution, as calculated from existing data.

The partial volume for any solute may be determined from successive weighings of a picnometer filled with solutions of different concentrations. Let V be the volume in ccm. held by the picnometer, and let it contain M gm. of solution when the percentage concentration of the solute in question is $P \times 100$, and M' gm. of solution of concentration $P' \times 100$. The amount of solvent in the picnometer when it is weighed containing solution of concentration P is $(1-P)M$, hence the volume of a solution of concentration P' containing the same amount of solvent would be $\frac{(1-P)M}{(1-P')M'}V$, and the amount of the solute in that solution would be $\frac{(1-P)M}{(1-P')M'}P'M'$ leading to the relation

$$\frac{\Delta v}{\Delta m} = \frac{\frac{(1-P)M}{(1-P')M'}V - V}{\frac{(1-P)M}{(1-P')M'}P'M' - PM} = \frac{(1-P)MV - (1-P')M'V}{(1-P)MP'M' - (1-P')M'PM} \quad (3)$$

It is evident that the percentage accuracy in the determination of this quantity $\Delta v/\Delta m$ will be greater the greater the quantities Δv and

TABLE III.

(Dec. 10, 1909.)

Solution: Molal LiI, $\frac{1}{100}$ molal I₂. $r_2 = 29.45$ cm., $r_1 = 4.2$ cm.Standardization of Magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 0.8605$ (6 exp.
av. dev. $\pm .0040$).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8605$ = rev. per sec.	$\frac{E}{n^2} \times 10^6$.	Dev. from mean.
10.10	0	-0.2
.24	0	-0.20
.29	0	-0.15
.33	0	-0.30
.36	59.2	+3.25	50.9	1253	+70
.36½	60.2	3.26	51.8	1217	+34
.37	61.2	3.30	52.6	1192	+9
.37½	61.5	3.30	52.9	1179	-4
.38½	61.9	3.31	53.3	1163	-20
.39	0	-0.20
.40	0	-0.5
.41½	0	-0.4
.44	0	-0.13
.45½	64.1	+3.65	55.1	1202	+19
.46	64.8	3.72	55.8	1193	+10
.46½	65.1	3.68	56.0	1172	-11
.47½	66.0	3.76	56.8	1165	-18
.48	66.3	3.77	57.1	1157	-26
.49	0	-0.15
.49½	0	-0.2
.50	0	-0.25
.51	0	-0.25
.51½	0	-0.25
.53	0	-0.22
.56	0	-0.25
.58½	69.5	+4.23	59.8	1182	-1
.59	69.3	4.22	59.6	1188	+5
.60	69.2	4.18	59.5	1180	-3
11.00½	68.7	4.13	59.1	1183	0
.01	68.4	4.05	58.8	1171	-12
.01½	68.3	4.04	58.75	1170	-13
.02½	0	-0.14
.03½	0	-0.18
.04	0	-0.14
.05½	0	+0.10
.07½	0	0.15
.09½	0	0.16
.11	0	0.09
.13	73.8	4.80	63.5	1190	+7
.13½	74.0	4.80	63.7	1182	-1
.14	74.0	4.75	63.7	1169	-4

TABLE III. — *Continued.*

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8605$ = rev. per sec.	$\frac{E}{n^2} \times 10^6$.	Dev. from mean.
.14 $\frac{1}{2}$	74.1	4.77	63.75	1173	-10
.15 $\frac{1}{2}$	74.5	4.84	64.1	1178	- 5
.16	74.8	4.85	64.4	1170	-13
.17	0	-0.19
.17 $\frac{1}{2}$	0	-0.27
.18	0	-0.30
.19	0	-0.30
.20 $\frac{1}{2}$	0	-0.28
.24	0	-0.32
.39	0	-0.36
...
...
...
.44	0	-0.20
.46	0	-0.03
.48	80.1	+5.62	68.9	1184	+ 1
.48 $\frac{1}{2}$	79.8	5.61	68.7	1189	+ 6
.49	79.3	5.48	68.25	1177	- 6
.49 $\frac{1}{2}$	79.1	5.47	68.1	1179	- 4
.50 $\frac{1}{2}$	78.5	5.38	67.5	1180	- 3
.52	0	-0.16
.52 $\frac{1}{2}$	0	-0.25
.53 $\frac{1}{2}$	0	-0.30
.55	0	-0.25
.56 $\frac{1}{2}$	0	-0.25
.58	0	-0.25
12.00	84.1	+6.30	72.4	1202	+19
.00 $\frac{1}{2}$	84.5	6.33	72.7	1198	+15
.01	84.1	6.18	72.4	1180	- 3
.02	84.0	6.15	72.25	1178	- 5
.02 $\frac{1}{2}$	84.1	6.16	72.4	1175	- 8
.03	0	-0.18
.04	0	-0.35
.04 $\frac{1}{2}$	0	-0.35
.05 $\frac{1}{2}$	0	-0.25
.06 $\frac{1}{2}$	0	-0.07
.09 $\frac{1}{2}$	0	+0.15
Average				1183	± 11.7

TABLE IV.
(Nov. 20, 1909.)Solution: Molal HI, approx. $\frac{M}{50} I_2$. $r_2 = 29.43$ cm., $r_1 = 4.51$ cm.Standardization of Magneto: $-\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 1.0125$ (6 exp.
av. dev. $\pm .0095$).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.0125$ = rev. per sec.	$\frac{E}{n^2} \times 10^6$.	Dev. from mean.
10.53	0	-0.38
11.10	0	-0.45
.17	0	+0.50
.18½	63.0	1.55	63.8	380	+ 4
.19½	70.0	1.83	70.8	365	- 11
.20	70.2	1.90	71.0	377	+ 1
.20½	70.0	1.90	70.8	379	+ 3
.21½	0	-0.17
.22½	0	-0.25
.24	0	-0.22
.25	0	-0.15
.26	0	-0.1
.28	0	-0.08
.29½	73.5	+2.13	74.4	385	+ 9
.30½	76.0	2.17	76.9	367	- 9
.30	76.1	2.25	77.0	379	+ 3
.31½	75.5	2.25	76.4	385	+ 9
.32	75.8	2.25	76.7	382	+ 6
.33	0	-0.12
.33½	0	-0.20
.35	0	-0.16
.36½	0	-0.12
.38 (?)	0	-0.01
.45	78.5	+2.35	79.4	373	- 3
.46	79.0	2.33	79.9	365	- 11
.46½	78.5	2.40	79.4	381	+ 5
.47	78.2	2.35	79.1	376	0
.48	0	-0.10
.48½	0	-0.15
.49½	0	-0.15
.50½	0	-0.10
.52	0	-0.07
.53	0	-0.02
.54½	79.0	+2.45	79.9	384	+ 8
.55	80.5	2.45	81.4	370	- 6
.56	81.0	2.45	81.9	366	- 10
.57	0	-0.10
.57½	0	-0.15
.58	0	-0.15
.60	0	-0.07
12.03	0	+0.06
Average				375.9	± 6.1

Δm ; in other words, the farther apart the concentrations P and P' are taken. On the other hand, if we are interested in the partial volume of the solute at the concentration P , we must determine the limit of $\Delta v/\Delta m$ as P' is brought nearer and nearer to P . A satisfactory solution of the problem may often be obtained by determining $\Delta v/\Delta m$ for several different values of P' , if possible making it in some cases larger and in others smaller than P . These values will then permit a close estimate of the limit of $\Delta v/\Delta m$ at the concentration P .

If a calculation of the quantity $\Delta v/\Delta m$ from specific gravity data is desired, equation (3) has to be changed merely by the substitution of the densities d and d' for the weights M and M' and by placing the volume V equal to unity, giving the formula

$$\frac{\Delta v}{\Delta m} = \frac{(1 - P)d - (1 - P')d'}{(1 - P)dP'd' - (1 - P')d'Pd} \quad (4)$$

For the purpose of determining the partial volume of iodine in iodide solutions picnometer weighings were made of a solution of approximately quarter normal potassium iodide containing varying quantities of iodine. The partial volume was desired in solutions very dilute in iodine ($\frac{M}{1000} I_2$); and hence the solutions were made as dilute in iodine as was consistent with a reasonable degree of accuracy in the calculation of $\Delta v/\Delta m$ between pure potassium iodide solution and the iodine solution in question. It is especially desirable to make the determinations with solutions as dilute as the accuracy of the method will permit, since the exact measurements of Kohlrausch and Hallwachs¹⁷ have shown that for several substances there is a rapid change in partial volumes when considerable dilutions are reached.

For the measurements, two separate solutions were made up from the same KI solution each containing about 1.5% I_2 . The concentration of the solutions was determined by weighing the iodine used and transferring it directly from a glass-stoppered weighing tube into the solution. The amount of solution used was also determined by weight. From each of these original solutions two more were prepared by dilution with weighed quantities of the pure potassium iodide solution, giving in all six iodine solutions whose densities were determined. The density of the original KI solution was also determined.

The volume of the picnometer used was about 21 cc., and was exactly determined by weighing the picnometer filled with pure water. The

¹⁷ Wied. Ann. 53, 14 (1894).

picnometer used was of the form recommended by Ostwald and Luther and the setting of the meniscus in the capillary was made in a thermostat kept constant at 25° C. For each solution, at least two weighings were made, the picnometer being replaced in the thermostat and the meniscus reset between weighings. The weighings were made immediately after removing the picnometer from the thermostat and wiping off the surface. The successive weighings of the same solution usually agreed within two tenths of a milligram. Proper corrections were made for the buoyancy of the air. The iodine was prepared by re-subliming with potassium iodide.

The results are presented in the following table :

No. of Sol.	%I ₂	Density	$\Delta v/\Delta m$
1	1.630	1.03955	0.2370
2	1.506	1.03842	0.2390
1'	1.099	1.03525	0.2362
2'	1.014	1.03452	0.2410
1''	0.8292	1.03310	0.2385
2''	0.7538	1.03250	0.2374
0	0	0.02660	0

The last column gives the value $\Delta v/\Delta m$ between a solution containing no iodine and one of the concentration indicated. No evidence is present of a systematic variation of $\Delta v/\Delta m$ with the concentration. Omitting the value of $\Delta v/\Delta m$ for solution no. 2', the average value is $\Delta v/\Delta m = 0.2376 \pm 0.0004 \left(= \frac{\text{average dev.}}{\sqrt{5}} \right)$, and this was taken as the partial specific volume of iodine at great dilutions in potassium iodide solution. The specific volume of pure iodine from the data in Landolt and Börnstein is 0.202.

In the following tables the results are given for some calculations of $\Delta v/\Delta m$ for potassium, sodium, lithium and hydrogen iodides in aqueous solution at 20° C. from the data of Wegner and of Perkin given in Landolt and Börnstein.

POTASSIUM IODIDE (WEGNER).

$P \times 100.$	$P' \times 100.$	$d_{20.4}.$	$d'_{20.4}.$	$\Delta v / \Delta m.$
10.27	15.12	1.0784	1.1205	0.283
10.27	20.04	1.0784	1.1665	0.285
15.12	20.04	1.1205	1.1665	0.286

For a concentration of one mol per kg. water $P \times 100 = 14.2$, dv/dm taken as 0.284 cc.

Specific volume of the solid (L & B) 0.326 cc.

SODIUM IODIDE (WEGNER).

$P \times 100.$	$P' \times 100.$	$d_{20.4}.$	$d'_{20.4}.$	$\Delta v / \Delta m.$
6.25	9.28	1.0483	1.0743	0.240
6.25	14.70	1.0483	1.1239	0.242
9.28	14.70	1.0743	1.1239	0.244

For a concentration of one mol per kg. water $P \times 100 = 13.0$, dv/dm taken as 0.244 cc.

Specific volume of the solid (L & B) 0.282.

LITHIUM IODIDE (WEGNER).

$P \times 100.$	$P' \times 100.$	$d_{20.4}.$	$d'_{20.4}.$	$\Delta v / \Delta m.$
0	5.90	0.9997	1.0437	0.262
0	10.54	0.9997	1.0825	0.2615
5.90	10.54	1.0437	1.0825	0.261

For a concentration of one mol per kg. water $P \times 100 = 11.8$, dv/dm taken as 0.2605 cc.

Specific volume of the solid (L & B) 0.246.

HYDROGEN IODIDE (PERKIN).

$P \times 100.$	$P' \times 100.$	d_{20-20}	d'_{20-20}	$\Delta v / \Delta m.$
0	20.77	1.0000	1.1754	0.2815
0	31.77	1.0000	1.2962	0.2805
20.77	31.77	1.1754	1.2962	0.2795

For a concentration of one mol per kg. water $P \times 100 = 11.3$, dv/dm taken as 0.2815 cc. (20°) or 0.282 true cc.

It is interesting to note in the cases of potassium and sodium iodides that the specific volume of the pure substance is greater than the partial specific volume of the substance in solution, and in these cases there is a slight but definite increase in the partial volume as the solution becomes more concentrated, that is, as it approaches the pure salt. Moreover, in the case of lithium iodide, although here the partial volume in solution is greater than the volume of the pure substance it also approaches the latter as the solution becomes more concentrated.

9. CALCULATION OF THE TRANSFERENCE NUMBER.

Substituting for π its value, and for F the value 96580, equation (2) may be written :

$$T_c = \left(\frac{4.895 \times 10^{10} E}{(r_2^2 - r_1^2) n^2} + M_I (1 - v_I d) \right) \div M_s (1 - v_s d).$$

Using the average values of E/n^2 the transference number of the cation T_c was calculated for each of the salts. The data and results are given below :¹⁸

Solution.	$\frac{E}{n^2} \times 10^6.$	$(r_2^2 - r_1^2)$	M_s	v_s	M_I	v_{I_2}	d_s	T_c	P. E.
$\frac{M}{1} KI, \frac{M}{100} I_2$	657.1	846.0	166.0	0.284	126.9	0.2376	1.115	0.486	± 0.001
$\frac{M}{1} NaI, \frac{M}{100} I_2$	889.0	849.3	149.9	0.244	126.9	0.2376	1.110	0.385	± 0.001
$\frac{M}{1} LiI, \frac{M}{100} I_2$	1183.	849.3	133.9	0.2605	126.9	0.2376	1.096	0.268	± 0.0013
$\frac{M}{1} HI, \frac{M}{100} I_2$	375.9	846.2	127.9	0.282	126.9	0.2376	1.090	0.816	± 0.001

¹⁸ The values of E/n^2 are, of course, all negative since the current tends to flow from the outer to the inner electrode.

The Accuracy of the Results.

The last column in the table gives the extremely small "probable error" introduced into the value of the transference number, by the deviations between the different measurements of E/n^2 . It was obtained by dividing the mean deviations by the square root of the number of observations. It is not a satisfactory measure of the reliability of the transference numbers, since there is considerable probability that the "residual" electromotive force existing between the electrodes during rotation were more likely to be in one direction than the other. The value ± 0.010 may be taken as a fairer measure of the probable accuracy of the determinations. In the case of KI, this would correspond to an average error of about 0.1 millivolt in the electromotive force.

The Effect of Pressure on the Results.

In deriving the equation on page 114 for the potential difference of a cell under the influence of centrifugal force, the tacit assumption was made that the quantities v_s , v_I , and d are, throughout the solution, the same as those calculated from density measurements made at atmospheric pressure. This is not strictly true, since there is considerable pressure produced in the solution by the centrifugal force. The following equation in which the quantities are considered as variables is exact.

$$10^7 EF = \int_{r_1}^{r_2} 4\pi^2 n^2 r [T_c M_s (1 - v_s d) - M_I (1 - v_I d)] dr \quad (5)$$

The derivation of the equation is obvious. $10^7 EF$ is the external work obtained when one faraday of electricity flows through the solution under the potential difference E produced by the centrifugal action. This quantity of energy is equal to the work required to restore the solution to its original condition. To accomplish this $T_c M_s$ gm. of salt must be brought back from r_2 to r_1 , and this quantity, multiplied by $v_s d$, is the number of gm. of displaced solution which will automatically move in the opposite direction as we move the salt through the solution, M_I and $v_I d$ are the same quantities for the iodine, which has to be transferred from r_1 to r_2 . The centrifugal force acting on the material which is to be moved is the product of the mass into $4\pi^2 n^2 r$ and the total work done is obtained by multiplying by dr , and integrating between r_2 and r_1 . If the integration is made on the assumption that v_s , v_I , and d do not vary with r , that is, with the pres-

sure, the equation actually used is obtained. As a matter of fact both the density of the solution and the partial volume of the salt will vary with the pressure, and hence as we move the salt through the solution from one electrode to the other at each level it will displace a different weight of solution, and will hence be buoyed up by a different amount. We have no data for the variation of v_s and v_{I_s} with the pressure, but an upper limit for the error which has been introduced by taking them as constant, may be calculated.

Assuming that $v_s d$ and $v_{I_s} d$ vary linearly with the pressure, since the pressure equals $2\pi^2 n^2 r^2 d$ ¹⁹ where d is approximately unity, we may write the equations

$$v_s d = \underline{v_s d}_0 (1 + 2\pi^2 n^2 r^2 a_1),$$

$$v_{I_s} d = \underline{v_{I_s} d}_0 (1 + 2\pi^2 n^2 r^2 a_2),$$

where $\underline{v_s d}_0$ and $\underline{v_{I_s} d}_0$ are the values for zero pressure, and a_1 and a_2 are the linear coefficients for the fractional change of $v_s d$ and $v_{I_s} d$ with the pressure. Substituting into equation (5) and integrating we obtain

$$E = \frac{2\pi^2 n^2}{10^7 F} (r_2^2 - r_1^2) [T_c M_s (1 - \underline{v_s d}_0) - M_I (1 - \underline{v_{I_s} d}_0)] \\ - \frac{2\pi^4 n^4}{10^7 F} (r_2^4 - r_1^4) (T_c M_s a_1 \underline{v_s d}_0 - M_I a_2 \underline{v_{I_s} d}_0).$$

The second term in the expression is seen to be the error introduced into the calculation of the electromotive force, by neglecting the change of the density and partial volumes with the pressure. Since the partial volumes will probably decrease with pressure and partly neutralize the increase in density, to obtain an upper limit for the error let us put a_1 and $a_2 = 4 \times 10^{-12}$, the value for the fractional change in the density of water per $\frac{\text{dyne}}{\text{cm}^2}$. Making this substitution, the value of the above term becomes only 0.00018 millivolts, for the experiment on potassium iodide, at 80 revolutions per second. We see that no appreciable error has been introduced by neglecting the change in the density and the partial volumes produced by pressure.

Before leaving the consideration of the pressure gradient in the tube, it must be pointed out that the transference number determined in these experiments is the transference number which exists when the solution is actually under the influence of that particular pressure gra-

¹⁹ This is strictly true only when the liquid reaches way to the center of the rotating apparatus.

dient. Owing to their enormous "internal pressure" the properties of liquids are, however, in general but little affected by changes in the external pressure.

The Effect of the Dissolved Iodine on the Results.

In the case of the alkali iodides one per cent of the \bar{I} ion was changed into \bar{I}_2 ion by the iodine present. In the HI solution, owing to oxidation about twice as much iodine was present. The transference number would, however, be only slightly affected by the small admixture of \bar{I}_2 ion.²⁰

10. COMPARISON OF THE RESULTS WITH OTHER TRANSFERENCE MEASUREMENTS.

The available data on the transference numbers of iodides are very few, and, of these, many are vitiated by the use of membranes in the apparatus.²¹ The most satisfactory data for comparison are the values determined by Washburn²² for the Hittorf transference numbers of the alkali chlorides (at a concentration 1.2 — 1.3 molal), and the value for the Hittorf transference number of hydrochloric acid (at a concentration 1.0 molal) which can be calculated from Buchböck's determination of true transference number and hydration. This comparison is made in Table V. The transference numbers for the chlorides and iodides at infinite dilution, calculated from conductivity data are also given in the table, and finally, values obtained for $\frac{N}{10}$ KI and $\frac{N}{10}$ NaI by Dennison²³ using the method of Dennison and Steele and a value by Bein²⁴ for $\frac{N}{20}$ KI. This last is the only available datum for these iodides obtained by the Hittorf method without the use of membranes.

²⁰ For data on the mobility of the I_2 ion see Burgess & Chapman, J. Chem. Soc. Trans. **85**, 1305 (1904), Bray & MacKay, Journ. Amer. Chem. Soc., **32**, 914 (1910).

²¹ See McBain (Proc. Wash. Acad. Sci. **9**, 1-78 (1907); University of Toronto Studies, Papers from the Chem. Laboratories, No. 67, for a complete collection of the experimental data on transference numbers.

²² Washburn, Tech. Quart. **21**, 164 (1908); Journ. Amer. Chem. Soc., **31**, 322 (1909); Buchböck, Z. physik. Chem. **55**, 563 (1906).

²³ Dennison, Trans. Faraday Soc., **5**, 165 (1909). It has been shown by Lewis, J. Am. Chem. Soc. **32**, 862 (1910), that the method of Dennison and Steele gives, after applying a calculable correction, the Hittorf transference number and not the true transference number as stated by Washburn.

²⁴ Bein, Z. physik. Chem. **27**, 1 (1898).

TABLE V.

TRANSFERENCE NUMBER OF THE ANION.

Halide of	Iodide, Centrifugal.	Chloride, Washburn. Buchböck.	Iodide, Infinite Dilution. ²⁵	Chloride, Infinite Dilution. ²⁵	Iodide, Dennison.	Iodide, Bein.
K	0.514	0.518	0.507	0.503	0.514	0.505
Na	0.615	0.634	0.604	0.601	0.624
Li	0.732	0.722	0.665	0.662
H	0.184	0.160 ²⁶	0.174	0.172

The agreement between the results presented in the table for the iodides with those for the chlorides is satisfactory. The greatest deviation occurs in the values for the two halogen acids. Hydrochloric acid,²⁷ however, is known to be abnormal in its behavior since the transference number passes through a minimum at a concentration below normal, and the same effect might occur in hydriodic acid solution. Furthermore, since the electromotive force measured was so small in the case of hydriodic acid any constant error in the nature of a residual electromotive force might have had a large effect.

11. SUMMARY.

In this article an apparatus and procedure have been described for determining transference numbers by the centrifugal method, first

²⁵ These values for the transference number at infinite dilution were calculated from the latest conductivity data of Kohlrausch, *Zt. f. Electrochem.* **13**, 333 (1907).

²⁶ This value for the Hittorf transference number of molal HCl is calculated from Buchböck's determination of true transference number and hydration by the relation connecting those quantities as developed by Washburn. Washburn himself gives 0.18 for the Hittorf transference of HCl, a value which was taken from Kohlrausch's tables, but it is probably considerably too high. For HCl, 0.97 molal, Riensenfeld u. Reinhold, *Zts. f. Phys. Chem.* **68**, 440 (1909), obtain the value 0.155, and Hopfgartner, *Zts. Phys. Chem.* **25**, 115 (1898), obtains 0.159 for 0.9 molal HCl.

²⁷ Riensenfeld u. Reinhold, *Zts. f. phys. Chem.* **68**, 440 (1909).

tried by Des Coudres. The method consists in the measurement of the electromotive force produced between electrodes placed at the central and peripheral ends of a rotating tube containing the electrolyte. An equation can be derived, connecting this electromotive force and the transference number of the salt with the speed of rotation, the density of the solution, and the molecular weight and the "partial" specific volume of the substances involved, quantities which can be independently determined.

Some of the details of the construction of the rotating apparatus may have general interest. A distinctive feature of the apparatus was the method of driving the rotator as a "spinning top," which had not been specially balanced and which was hung below its fixed point of support. A simple arrangement of cords was devised for steadying the shaft of the rotating top and preventing precessional motion. A thrust bearing suitable for high speeds is also described. It consists of a series of ball bearings which distribute the total relative motion. An equation is given for calculating the dimensions of a rotating arm of uniform strength with the cross section increasing in size towards the center of rotation.

With this apparatus measurements were made of the electromotive force produced by the rotation of molal solutions of potassium, sodium, lithium, and hydrogen iodides. As predicted from the equations, the electromotive force was found to increase proportionately to the square of the speed of rotation. From the data the transference number was calculated for the four solutions, and found to agree as well as could be expected, with the available results of other methods of determination.

It was pointed out in connection with a kinetic derivation of the electromotive force relation, that the production of an electromotive force by centrifugal force is a proof of the presence of free ions in an electrolytic solution or at least of a certain degree of electrical polarization in the molecules.

The writer desires to express his gratitude to Professor A. A. Noyes, the Director of the Research Laboratory, whose interest and support made possible the completion of this research. Thanks are also due to Professor Elihu Thomson and Dr. Sanford A. Moss of the General Electric Company, through whose kind offices was loaned the steam turbine used in this investigation. The writer also had the benefit of Dr. Moss's extensive experience with high-speed rotation, and is indebted to Professor George B. Haven of the Institute for his assistance in checking a large number of calculations of machine design which were made before the final apparatus was constructed.

The construction of the apparatus was made with the help of two grants of money from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences. The Chemical Department of the Institute was also very generous in its support of this costly research.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., June, 1910.

